[Second Edition.]

PATENT SPECIFICATION

Application Date: July 7, 1924. No. 16,275/24.

238,663

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PROVISIONAL SPECIFICATION.

Improvements relating to Extraction of Metals from their Compounds.

I, ALFRED STUART CACHEMAILLE, of 2, Norfolk Street, Strand, London, W.C. 2, a subject of the King of Great Britain, do hereby declare the nature of this invention to be as follows:—

This invention relates to methods of obtaining metals from their compounds and more particularly from their oxides.

It has been proposed to obtain the powders of metals, the oxides of which cannot be reduced to metal by means of hydrogen, for example the oxides of uranium, zirconium, thorium, vanadium, tantalum, chromium, titanium, *etc.*, or any other similarly difficultly reducible oxide, by well known metallurgical processes, one of which involved the reduction of the oxides by means of calcium. Attempts have also been made to reduce the oxides of certain of the metals mentioned by the alkali metals, but without success. The calcium method is open to objection because of the relative expensiveness of that metal and the impurities contained in the commercial material, also because the heat of reaction is high which causes coarseness of the powders through the agglomerations of the particles thereof. In order to render effective the alkali metal reduction a further proposal has been made to employ an alkali metal as the reducing agent, together with a fluxing agent such as an alkaline earth halide or an alkali metal halide of a metal other than the alkali metal employed as the reducing agent. This method has been very successful, although open to several objections when it is the desire to obtain a very fine powder possessing a certain fineness. In practising the methods referred to above, it has been customary to insert the mixed ingredients in an iron bomb, and after sealing the latter, the reaction is started by heating the bomb. The iron, in some manner, finds its way into the metal produced, so that when the powder is sintered to reduce it to the coherent state, it forms, it is believed, with the iron, a low-melting point alloy which forms beads and runs out from the mass leaving cracks in the material and also causing a great deal of trouble in the furnace. Attempts have been made to prevent the introduction of the iron impurity by lining the bomb with nickel, copper, chromium, *etc.*, but in each case, metallic impurities were introduced which were most undesirable in preparing pure metals.

To illustrate the effect on the physical properties of a metal by the introduction of a small amount of an impurity, reference need only be made to the effect of carbon or any metallic impurity in pure iron. For example, a small amount of silicon or carbon, when introduced into iron, causes the latter to become hard and brittle. The same effect will probably be produced if instead of iron, say uranium or thorium, were used. From my correspondents' experience with the rare refractory metals and their preparation, they are convinced that when iron is present as an impurity, it is very difficult to obtain the metal with which it is combined in a solid coherent condition owing to the beading previously referred to. The object of the present invention is to obtain the rare refractory metal powders in a very pure state and of a predetermined degree of fineness for which purpose, according to the invention, an alkaline earth metal, preferably calcium is employed as the reducing agent and a halide of the same alkaline earth metal is employed as the fluxing agent, although the halides of other metals of the alkali or alkaline earth group of metals may be employed. A mixture of the metallic oxide to be reduced, the alkaline earth metal and the alkaline earth or alkali metal halide is formed, the reducing metal preferably being in about 50% excess of the theoretical quantity required. This mixture is heated in a suitable vessel, preferably a bomb, which is evacuated or

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provided with an inert atmosphere from which nitrogen and oxygen are absent.

In the accompanying drawing is illustrated a vertical sectional view, partly in elevation, of a bomb provided with an insulating lining of calcium oxide within which the charge is placed. The bomb comprises a hollow iron cylinder 2 having a chamber 3 within the same. The bomb may be about 10 inches in height and 4 inches in diameter with a wall thickness of approximately a half inch. The upper end 4 of the bomb is provided with an internal tapered thread 5 into which fits a tapered threaded plug 6 to the threads of which a sealing compound may be applied just previous to the insertion of the plug into the bomb. The inner walls of the chamber 3 in the bomb are preferably provided with an insulating layer 7 of calcium oxide or other refractory material which may preferably be applied in a manner more fully described hereinafter.

In placing the mixture into the bomb, the following precautions are observed in order to prevent the introduction of impurities from the bomb. The bottom 8 of the bomb is covered with a layer 9 of pure, highly ignited lime which contains no iron, silicon, or insoluble impurities. By insoluble impurities is meant insoluble in dilute acetic acid. After the bottom of the bomb has been covered about a quarter inch deep by thoroughly packing with a clean iron plunger, the mixture of calcium chloride, finely cut calcium, and the rare refractory metal oxide is pressed into cakes 11 somewhat smaller than the inside of the bomb. A cake is placed centrally on the lined bottom of the bomb and lime powder 12 is run in around the cake and packed down with a clean copper or iron ring. Usually, three or four cakes are pressed and put in, one at a time, the lime being packed around each one of them. after its introduction within the bomb, so that the final formation comprises an insulating layer of the lime interposed between the mixture and the walls of the bomb. A piece 13 of calcium is placed upon the uppermost cake to combine with the residual air remaining in the bomb or materials within the same. The bomb is then sealed by inserting the plug 6 after having previously applied a sealing mixture of magnesium oxide and linseed oil thereto. The bomb may be evacuated or provided with an inert environment, although this is not essential since the lump of calcium can remove the residual air. The reaction is then started by the external application of heat.

After the reaction is complete and the bomb permitted to cool, the contents thereof may be removed by means of a star drill which is small enough not to touch the sides of the bomb at any time and which has a stop on the handle so that the drill cannot come closer than $^1/_8$" of the bottom. In that way practically all of the charge is removed, but no iron is knocked loose from the bomb mechanically and practically no corrosion can take place or iron be introduced since there is no contact between the specimen and the metal of the bomb.

Also, alternatively, if the bomb and the contents are kept cool, the charge can be disintegrated with water, which process avoids the necessity of cutting loose the charge with a drill. Considerable care must be exercised to keep the bomb and contents cool, otherwise the purity of the rare metal powder, particularly in the case of uranium is destroyed by interaction with the hot water.

The contents of the bomb upon removal may be treated in any well known manner to remove the undesirable products of the reaction. For example, such purification may consist of washing with dilute acid, water, *etc.* so that only the pure metal powder remains.

The advantages of the process according to the invention are as follows. First, the alkaline earth metal halide may, with certain refractory oxides, serve as a flux so that the oxide is converted to the chloride, partially at least, from which it is readily reduced. Second, the powder which is formed usually settles to the bottom of the fused mass so that the fluid calcium chloride very effectually seals it away if any leakage in the bomb occurs after the reduction of the metal. Third, the calcium chloride serves as a medium so that the calcium and the oxide come very intimately into contact. The reduction, therefore, is very complete. Fourth, the alkaline earth metal halide or flux material slows up the reduction and thus provides a means for the regulation of the fineness of the powder by the excess of the fluxing agent, so that when the temperature of reduction and the excess of reducing agent are once determined, a high yield of the metal powder may be obtained of uniform fineness.

To enable those skilled in the art to practise the invention, one method of applying the principle involved will be described in detail, and for this purpose uranium oxide will be selected as an example of a difficultly reducible oxide, calcium as the alkaline earth metal or reducing agent, and calcium chloride as

the alkaline earth halide or fluxing agent.

An intimate mixture is prepared in any suitable manner of 92 parts by weight of uranium oxide (UO_2), or under slightly differing conditions equivalent quantities of the other oxides of uranium, a large excess (120 parts by weight) of calcium prepared from purified calcium chloride, and a suitable quantity or about 200 parts by weight of purified calcium chloride. The calcium chloride purchased as chemically pure and labelled "calcined" contains water, and in practising the process is preferably carefully dried at about 450° C. so that as employed it contains only a few tenths of one *per cent.* of moisture. If the commercial "calcined" calcium chloride is used, then it is necessary to employ an excess of calcium to combine with the oxygen. It is desirable to have very pure materials, since a small amount of iron for example, appears to cause beading due to the formation of low-melting point alloys, *etc.* Silicon also makes the metal hard and brittle.

The mixture is pressed into cakes somewhat smaller than the bomb into which they are placed. A lining of pure calcium oxide is placed around the cakes in the manner hereinbefore described, after which the bomb is sealed. The bomb may then be evacuated or provided with an inert atmosphere, or instead of this treatment a lump of calcium may be placed on top of the charge, prior to sealing of the bomb, to combine with any residual air remaining within the same. External heat is applied to raise the temperature of the bomb to about 900° C. or 1000° C. and this temperature is maintained from two to three hours. The actual temperature to which the bomb is heated depends upon the proportions of calcium and calcium chloride used, upon the duration of heating and upon the oxide used. For example, uranium oxide having the chemical formula UO_2 takes a different temperature, excess of reagents and time of heating than is required for the oxide having the formula U_3O_8.

After the completion of the reaction, the products are allowed to cool and are then removed from the container by means of a drill or disintegrated with water.

The following procedure has been followed in treating the products of the reaction to remove all but the rare refractory metal powder. The mass is disintegrated in water, the latter being constantly stirred so as to bring about a more intimate contact with the mass. After settling, the supernatant liquor is decanted, and the residue washed with fresh water. The washing treatment is repeated several times after which dilute acetic acid is added to the residue to remove matter soluble therein. The residue is then washed with water and the residue again acidified as before. The acid and water washing treatments are repeated about four times after which the residue is put through a suction filter and washed with distilled water. The distilled water washing in the filter is followed by washing with alcohol. The powder is partially dried by suction and it is then quickly put through a 200 mesh screen a little at a time. If the powder is exposed to the air for a short time, it frequently spontaneously ignites and is burned to oxide so that this must be done quickly. The powder is preserved by being placed in pure alcohol.

Many other methods may be followed in lining the bomb. For instance, the lining material may be pressed around a core, which latter may be withdrawn, or it may be wetted and painted in. Obviously other materials may be employed as the lining material, for example, strontium oxide. However, it should be remembered that the material employed for lining the bomb should be such as to avoid the introduction of impurities.

If so desired, when calcium and calcium chloride are used as reducing and fluxing agents, it is possible completely to remove the undesirable products of the reaction and the excess of reducing agents by means of pure alcohol and a solution of an acid in alcohol such as hydrogen chloride, thus avoiding the use of water and contamination due thereto.

In order to obtain pure refractory metal powders precautions must be taken to eliminate as far as is practically possible from the materials, such as the oxides, the calcium, the calcium chloride, the calcium oxide, and other reagents, any impurities, such as iron, free carbon, carbides, *etc.*, which may be present therein.

It is to be understood that various modifications can be made in the arrangements described without departing from the scope of the invention.

Dated the 7th day of July, 1924.

F. W. Le TALL,
Chartered Patent Agent,
2, Norfolk Street, Strand, London, W.C.,
Agent for the Applicant.

COMPLETE SPECIFICATION.

Improvements relating to Extraction of Metals from their Compounds.

I, Alfred Stuart Cachemaille, of 2, Norfolk Street, Strand, London, W.C. 2, a subject of the King of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to methods of obtaining metals from their compounds and more particularly from their oxides.

It has been proposed to obtain the powders of metals, the oxides of which cannot be reduced to metal by means of hydrogen, for example the oxides of uranium, zirconium, thorium, vanadium, tantalum, chromium, titanium, *etc.*, or any other similarly difficultly reducible oxide, by well known metallurgical processes, one of which involved the reduction of the oxides by means of calcium. Attempts have also been made to reduce the oxides of certain of the metals mentioned by the alkali metals, but without success. The calcium method is open to objection because of the relative expensiveness of that metal and the impurities contained in the commercial material, also because the heat of reaction is high which causes coarseness of the powders through the agglomerations of the particles thereof. In order to render effective the alkali metal reduction a further proposal has been made to employ an alkali metal as the reducing agent, together with a fluxing agent such as an alkaline earth halide or an alkali metal halide of a metal other than the alkali metal employed as the reducing agent. This method has been very successful, although open to several objections when it is the desire to obtain a very pure powder possessing a certain fineness. In practising the methods referred to above, it has been customary to insert the mixed ingredients in an iron bomb, and after sealing the latter, the reaction is started by heating the bomb. The iron, in some manner, finds its way into the metal produced, so that when the powder is sintered to reduce it to the coherent state, it forms, it is believed, with the iron, a low-melting point alloy which forms beads and runs out from the mass leaving cracks in the material and also causing a great deal of trouble in the furnace. Attempts have been made to prevent the introduction of the iron impurity by lining the bomb with nickel, copper, chromium, *etc.*, but in each case, metallic impurities were introduced which were most undesirable in preparing pure metals.

To illustrate the effect on the physical properties of a metal by the introduction of a small amount of an impurity, reference need only be made to the effect of carbon or any metallic impurity in pure iron. For example, a small amount of silicon or carbon, when introduced into iron, causes the latter to become hard and brittle. The same effect will probably be produced if instead of iron, say uranium or thorium, were used. From my correspondents' experience with the rare refractory metals and their preparation, they are convinced that when iron is present as an impurity, it is very difficult to obtain the metal with which it is combined in a solid coherent condition owing to the beading previously referred to. The object of the present invention is to obtain the rare refractory metal powders in a very pure state and of a predetermined degree of fineness for which purpose, according to the invention, an alkaline earth metal, preferably calcium is employed as the reducing agent and a halide of the same alkaline earth metal is employed as the fluxing agent, although the halides of other metals of the alkali or alkaline earth group of metals may be employed. A mixture of the metallic oxide to be reduced, the alkaline earth metal and the alkaline earth or alkali metal halide is formed, the reducing metal preferably being in about 50% excess of the theoretical quantity required. This mixture is heated in a suitable vessel, preferably a bomb, which is evacuated or provided with an inert atmosphere from which nitrogen and oxygen are absent.

In the drawing accompanying the provisional specification is illustrated a vertical sectional view partly in elevation of a bomb provided with an insulating lining of calcium oxide within which the charge is placed. The bomb comprises a hollow iron cylinder 2 having a chamber 3 within the same. The bomb may be about 10 inches in height and 4 inches in diameter with a wall thickness of approximately a half inch.

The upper end 4 of the bomb is provided with an internal tapered thread 5 into which fits a tapered threaded plug 6 to the threads of which a sealing compound may be applied just previous to the insertion of the plug into the bomb. The inner walls of the chamber 3 in the bomb are preferably provided with an insulating layer 7 of calcium oxide or other refractory material which may preferably be applied in a manner more fully described hereinafter.

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After the reaction is complete and the bomb permitted to cool, the contents thereof may be removed by means of a star drill which is small enough not to touch the sides of the bomb at any time and which has a stop on the handle so that the drill cannot come closer than $^1/_8$" of the bottom. In that way practically all of the charge is removed, but no iron is knocked loose from the bomb mechanically and practically no corrosion can take place or iron be introduced since there is no contact between the specimen and the metal of the bomb.

Also, alternatively, if the bomb and the contents are kept cool, the charge can be disintegrated with water, which process avoids the necessity of cutting loose the charge with a drill. Considerable care must be exercised to keep the bomb and contents cool, otherwise the purity of the rare metal powder, particularly in the case of uranium is destroyed by interaction with the hot water.

The contents of the bomb upon removal may be treated in any well known manner to remove the undesirable products of the reaction. For example, such purification may consist of washing with dilute acid, water, *etc.* so that only the pure metal powder remains.

The advantages of the process according to the invention are as follows. First, the alkaline earth metal halide may, with certain refractory oxides, serve as a flux so that the oxide is converted to the chloride, partially at least, from which it is readily reduced. Second, the powder which is formed usually settles to the bottom of the fused mass so that the fluid calcium chloride very effectually seals it away if any leakage in the bomb occurs after the reduction of the metal. Third, the calcium chloride serves as a medium so that the calcium and the oxide come very intimately into contact. The reduction, therefore, is very complete. Fourth, the alkaline earth metal halide or flux material slows up the reduction and thus provides a means for the regulation of the fineness of the powder by the excess of the fluxing agent, so that when the temperature of reduction and the excess of reducing agent are once determined, a high yield of the metal powder may be obtained of uniform fineness.

To enable those skilled in the art to practise the invention, one method of applying the principle involved will be described in detail, and for this purpose uranium oxide will be selected as an example of a difficultly reducible oxide, calcium as the alkaline earth metal or reducing agent, and calcium chloride as the alkaline earth halide or fluxing agent.

An intimate mixture is prepared in any suitable manner of 92 parts by weight of uranium oxide (UO_2), or under slightly differing conditions equivalent quantities of the other oxides of uranium, a large excess (120 parts by weight) of calcium prepared from purified calcium chloride, and a suitable quantity or about 200 parts by weight of

purified calcium chloride. The calcium chloride purchased as chemically pure and labelled "calcined" contains water, and in practising the process is preferably carefully dried at about 450° C. so that as employed it contains only a few tenths of one *per cent.* of moisture. If the commercial "calcined" calcium chloride is used, then it is necessary to employ an excess of calcium to combine with the oxygen. It is desirable to have very pure materials, since a small amount of iron for example, appears to cause beading due to the formation of low-melting point alloys, *etc.* silicon also makes the metal hard and brittle.

The mixture is pressed into cakes somewhat smaller than the bomb into which they are placed. A lining of pure calcium oxide is placed around the cakes in the manner hereinbefore described, after which the bomb is sealed. The bomb may then be evacuated or provided with an inert atmosphere, or instead of this treatment a lump of calcium may be placed on top of the charge, prior to sealing of the bomb, to combine with any residual air remaining within the same. External heat is applied to raise the temperature of the bomb to about 900° C. or 1000° C. and this temperature is maintained from two to three hours. The actual temperature to which the bomb is heated depends upon the proportions of calcium and calcium chloride used, upon the duration of heating and upon the oxide used. For example, uranium oxide having the chemical formula UO_2 takes a different temperature, excess of reagents and time of heating than is required for the oxide having the formula U_3O_8.

After the completion of the reaction, the products are allowed to cool and are then removed from the container by means of a drill or disintegrated with water.

The following procedure has been followed in treating the products of the reaction to remove all but the rare refractory metal powder. The mass is disintegrated in water, the latter being constantly stirred so as to bring about a more intimate contact with the mass. After settling, the supernatant liquor is decanted, and the residue washed with fresh water. The washing treatment is repeated several times after which dilute acetic acid is added to the residue to remove matter soluble therein. The residue is then washed with water and the residue again acidified as before. The acid and water washing treatments are repeated about four times after which the residue is put through a suction filter and washed with distilled water. The distilled water washing in the filter is followed by washing with alcohol. The powder is partially dried by suction and it is then quickly put through a 200 mesh screen a little at a time. If the powder is exposed to the air for a short time, it frequently spontaneously ignites and is burned to oxide so that this must be done quickly. The powder is preserved by being placed in pure alcohol.

The powder thus produced readily passes a 200 mesh sieve and can be pressed into hard solid cakes having much the appearance of molybdenum under the same conditions. It might be stated that when the powder is too fine it can be filtered only with difficulty and when pressed squeezes out at the sides of the press. When the powder is too fine, it is extremely difficult to degasify in the furnace since the large volume of gas causes cracks to be produced even when extreme care is exercised. It is usually necessary to press and handle pure uranium powder wet with alcohol in order to avoid spontaneous combustion in the air. Also a powder which is too fine shrinks to a large extent in the furnace, yielding misshapen slugs or buttons. When a powder is too coarse it does not hold its shape after pressing, but crumbles and can be handled only with difficulty.

Many other methods may be followed in lining the bomb. For instance, the lining material may be pressed around a core, which latter may be withdrawn, or it may be wetted and painted in. Obviously other materials may be employed as the lining material, for example, strontium oxide. However, it should be remembered that the material employed for lining the bomb should be such as to avoid the introduction of impurities.

If so desired, when calcium and calcium chloride are used as reducing and fluxing agents, it is possible completely to remove the undesirable products of the reaction and the excess of reducing agents by means of pure alcohol and a solution of an acid in alcohol such as hydrogen chloride, thus avoiding the use of water and contamination due thereto.

In order to obtain pure refractory metal powders precautions must be taken to eliminate as far as is practically possible from the materials, such as the oxides, the calcium, the calcium chloride, the calcium oxide, and other reagents, any impurities, such as iron, free carbon, carbides, *etc.*, which may be present therein.

It is to be understood that various modifications can be made in the

arrangements described without departing from the scope of the invention.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The manufacture of a metal from its oxide by heating the oxide with an alkaline earth metal and a halogen compound of an alkaline earth or an alkali metal.

2. The manufacture of a metal from its oxide by heating the oxide with calcium and calcium chloride.

3. The manufacture of a metal from its oxide according to Claims 1 or 2 in which the reaction is carried out in a vacuum or in an inert atmosphere.

4. The manufacture of a metal according to Claims 1 to 3, in which the fineness of division of the metal produced is controlled by adjusting the duration of heating and the proportions of the alkaline earth metal and the halogen compound used.

5. The manufacture of a metal which comprises forming a mixture of its oxide with an alkaline earth metal and a halogen compound of the same or other alkaline earth metal, enclosing said mixture in a bomb from which oxygen and nitrogen are excluded, raising the temperature of the bomb to a predetermined value for a definite time, cooling the bomb and then extracting the metal from the reaction products.

6. For the manufacture of a metal according to any of the preceding claims, a metallurgical bomb the walls of which are lined with a material which prevents the reduced metal being contaminated by the introduction of impurities from the material of the bomb.

7. A metallurgical bomb according to Claim 6 lined with calcium oxide.

8. The manufacture of a metal from its oxide substantially as described.

9. The manufacture of uranium from its oxide substantially as described.

Dated the 9th day of March, 1925.

F. W. LE TALL,
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Agent for the Applicant.

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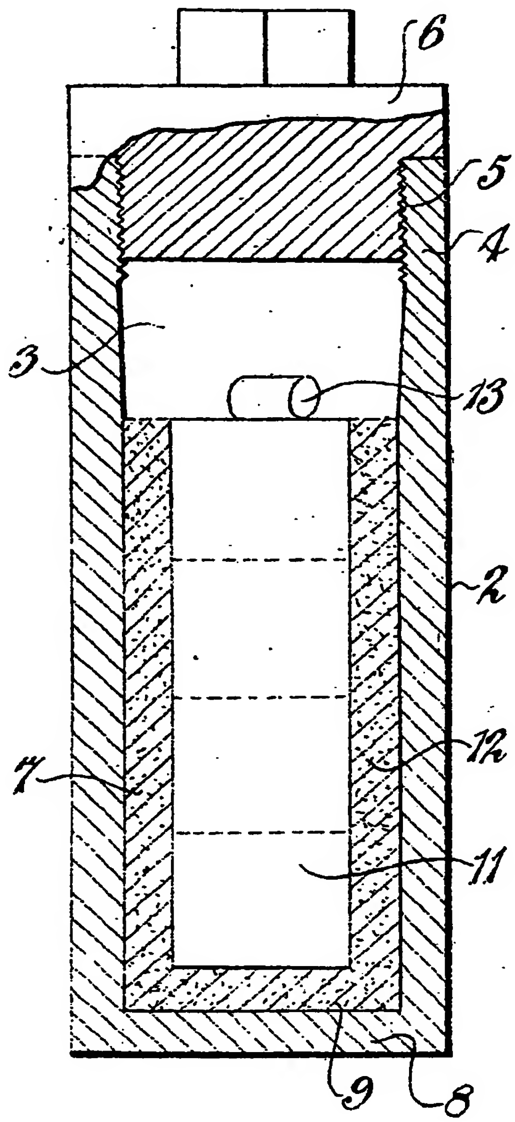
[Wt. 123A.—50/3/1932.]

2nd Edition

[This Drawing is a full-size reproduction of the Original]



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